Contributions to the Study of Heats of Adsorption of Gases and Heats of Gaseous Reactions on Catalyst Surfaces

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Contributions to the Study of Heats of Adsorption of Gases and Heats of Gaseous Reactions on Catalyst Surfaces

A DISSERTATION

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EARL WILLIAM FLOSDORF

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HEATS OF ADSORPTION ON CATALYTICALLY ACTIVE SURFACES*

BY EARL W. FLOSDORF

Quantitative measurements of the heats of adsorption of gases on catalytically active surfaces carried out in recent years[1] have established three main facts: inconstancy of the heats of adsorption, which suggests inhomogeneity of the surface; their magnitude, which proves that the adsorption is not of capillary nature but involves forces similar in nature to chemical bonds; the presence of minima in the heats of adsorption plots. This last phenomenon has not yet received a satisfactory theoretical interpretation, but its physical reality can hardly be doubted, being recorded already by a number of independent observers, with nickel, copper and charcoal as adsorbents and hydrogen, oxygen, carbon monoxide, sulphur dioxide and nitric oxide as adsorbates.

The present work was undertaken to extend the study of the heats of adsorption to a new class of adsorbents: metallic oxides. It includes in addition measurements on supported and non-supported platinum blacks, the latter being carried out with the purpose of checking those discrepancies between the heats of adsorption and the rates of evaporation from the platinum surface which have been noticed earlier by one of us (see Ref. 1).

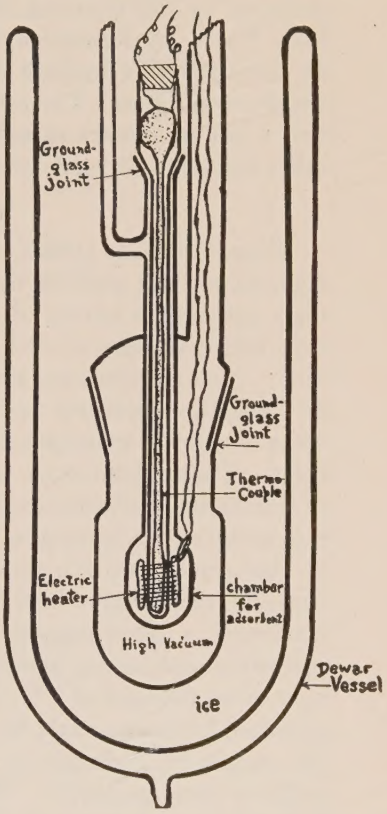

FIG. 1

Experimental Details

The method used here is in general very similar to the one described earlier by one of us[2] except for the calorimeter proper. The main change in the design of this latter consisted in substitution of a multiple thermocouple instead of the Pt-resistance thermometer. The design of the calorimeter should be clear from the accompanying diagram. The thermocouple con-

* Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, N. J.

[1] See Guy B. Taylor, George B. Kistiakowsky and John H. Perry: J. Phys. Chem., 34, 748 (1930). These refer to earlier literature.

[2] H. S. Taylor and G. B. Kistiakowsky: Z. physik. Chem., 125, 341 (1927).

sisted of 22 copper-constantan junctions insulated by silk and rubber, the whole forming a rod of about 7 mm. diameter and 20 cm. long.

With the new calorimeter fully as accurate results were obtained as with the old design but a far greater simplicity of operation was achieved.

The Adsorbents

The oxide catalyst studied was a zinc-chromium oxide preparation made by precipitating zinc chromate from a zinc oxalate solution by sodium chromate and by washing and igniting it. This preparation was identical in composition and structure with the material whose adsorption characteristics have been investigated by Taylor and Kistiakowsky.[3] Two supported and one non-supported platinum blacks were used. The supported blacks were prepared by precipitating platinum on asbestos from platinic chloride solution, No. 1, by formaldehyde in boiling caustic soda solution and No. 2 by hot hydrazine hydrate solution. These adsorbents contained 10% by weight of platinum. The unsupported black was prepared as the supported No. 1 but in absence of asbestos from a C.P. grade of platinum, while the other samples were made of technical grade.

Experimental Results

Zinc-Chromium Oxide. Considerable complications were caused in the beginning of the work on the zinc-chromium oxide preparation by the seemingly irreversible nature of adsorption. A fresh sample was found to adsorb very little hydrogen at 0°C., while it absorbed large quantities of this gas at 100°. Thus adsorbed gas could not be removed from the surface by pumping at higher temperatures except in the form of water vapor and the sample, when treated in hydrogen at 100° for longer time intervals, became green in color. These phenomena were undoubtedly caused by a partial reduction of zinc-chromium oxide and it appears most probable that in Taylor and Kistiakowsky's experiments on the adsorptive characteristics of this substance at least some hydrogen reacted chemically with the adsorbent. On treating zinc-chromium oxide with hydrogen at 300° until no more gas was being consumed, a green material was ultimately obtained which proved to be a reversible and strong adsorbent for hydrogen. The adsorption was found now to be stronger at 0°C. than at 100° and on heating the samples to 400° adsorbed hydrogen could be recovered as such quantitatively. Reduction of the sample by hydrogen at 300° affected the heat effects accompanying adsorption very markedly. While on a fresh unreduced sample values of the order of 60,000 cal per mol of hydrogen were observed, the heats of adsorption on the reduced samples amounted to some 20,000 cal. and less. From the foregoing discussion it is clear that the larger of these values is really a measure not of the heat of adsorption but of the heat of reduction of the chromium oxide. In the following are presented five consecutive series of measurements on a sample weighing 15 g. which was previously fully reduced by hydrogen at 300°. In these and in the following tables the data in the

[3] J. Am. Chem. Soc., 49, 2458 (1927).

first column are the volumes of hydrogen admitted into the calorimeter, in the second the resulting pressure increases, in the third the adsorbed volumes and in the fourth heats of adsorption in calories per mol of hydrogen. The last two columns show the total hydrogen pressure ten minutes after each gas admission and the total volume of gas adsorbed on 100 g. of adsorbent.

TABLE I

Reduced Zinc-Chromium Oxide
In vacuum for three hours at 400°

1	2	3	4	5	6
0.24	0.032	0.235	13.0	0.032	1.53
0.23	0.05	0.232	13.6	0.077	2.94
0.24	0.09	0.227	12.5	0.142	4.47
0.24	0.12	0.222	11.9	0.262	5.87
0.24	0.195	0.211	8.0	0.46	7.75
0.24	0.10	0.216	7.0	0.48	9.10

TABLE II

Reduced Zinc-Chromium Oxide
In vacuum for three hours at 400°

1	2	3	4	5	6
0.23	0.035	0.225	12.6	0.035	1.50
0.24	0.10	0.225	13.9	0.14	3.00
0.24	0.20	0.210	14.6	0.275	4.47
0.24	0.35	0.190	13.8	0.40	5.87
0.24	0.31	0.190	13.5	0.46	7.46
0.24	0.46	0.170	13.3	0.81	8.73
0.24	0.55	0.160	11.0	1.33	9.80

TABLE III

Reduced Zinc-Chromium Oxide
In vacuum for three hours at 400°

1	2	3	4	5	6
0.24	0.02	0.237	12.2	0.021	1.60
0.24	0.06	0.231	14.4	0.12	3.00
0.24	0.12	0.222	14.5	0.18	4.55
0.25	0.14	0.229	15.3	0.25	6.14
0.24	0.17	0.215	16.6	0.32	7.67
0.24	0.20	0.210	17.7	0.39	9.30
0.24	0.29	0.197	15.8	0.60	10.6
0.24	0.45	0.188	10.25	0.55	12.3
0.24	0.47	0.170	8.30	0.77	13.6
0.25	0.60	0.161	6.67	0.96	15.1
0.25	0.71	0.147	6.0	1.16	16.5

TABLE IV

Reduced Zinc-Chromium Oxide
In vacuum for three hours at 400°

1	2	3	4	5	6
0.23	0.018	0.227	18.0	0.018	1.50
0.24	0.046	0.233	19.5	0.064	3.00
0.23	0.09	0.217	19.9	0.14	4.47
0.24	0.12	0.222	18.5	0.22	5.93
0.24	0.14	0.219	15.9	0.31	7.40
0.24	0.18	0.213	15.0	0.36	8.95
0.24	0.245	0.203	15.8	0.47	10.40
0.24	0.24	0.204	13.9	0.57	11.8
0.23	0.52	0.153	14.3	0.84	13.1
0.24	0.52	0.163	11.0	1.00	14.5

TABLE V

Reduced Zinc-Chromium Oxide
In vacuum for three hours at 400°

1	2	3	4	5	6
0.23	0.015	0.228	15.4	0.015	1.47
0.23	0.04	0.224	14.6	0.05	2.92
0.23	0.07	0.221	13.3	0.12	4.33
0.24	0.16	0.216	12.2	0.27	5.86
0.23	0.22	0.197	12.0	0.37	7.20
0.23	0.23	0.196	10.9	0.40	8.68
0.23	0.40	0.170	10.6	0.57	10.0
0.24	0.49	0.180	10.3	0.77	11.3
0.27	0.55	0.190	8.5	0.95	13.3

It will be observed that repeated heatings in hydrogen to 400° with following degassings have marked influence on the heats of adsorption and on the total adsorptive capacity of zinc-chromium oxide. Both quantities change in quite a similar manner. The first treatments result in larger heats of adsorption and in an increased adsorptive capacity while towards the end of the series both start to diminish again. Parallel to these changes the formation and the following disappearance of a maximum in the heat curve can be observed from the tables. While the first table shows practically no indications of a maximum and in the fifth no maximum can be observed at all, in the third table, together with the maximal adsorptive capacity, a very well defined maximum is obtained which is reached only after adsorption of 9 cc. of hydrogen per 100 g. of adsorbent. The difference between the initial and the maximal value of the heat of adsorption amounts to some 5500 cal. per mol and is thus of the same order of magnitude as the differences obtained with copper.[4] The quantities of hydrogen adsorbed in the oxide surface at satura-

[4] Taylor and Kistiakowsky: loc. cit.

tion have not been determined here, all experiments having been discontinued at about 1 mm. pressure while adsorption was still very strong. The data here presented make it, however, most probable that the maximum point on the heat curve corresponds to a surface still very far from being saturated with hydrogen, in conformity with observations made on copper.

Supported platinum blacks. A sample of the black No. 1 weighing three grams was used for the measurements. It was degassed at 250°, treated for 2 hours with hydrogen at this temperature and degassed again. Several series of measurements were made with this sample with heat treatments at increasing temperatures between successive experiments. Of these series only the first and the last are presented in Tables VI and VII since the intermediate series fell smoothly between these two extremes.

TABLE VI

Supported Platinum Black No. 1

In vacuum for two hours at 250°

1	2	3	4	5	6
0.232	0.02	0.230	31.0	0.02	7.7
0.241	0.10	0.226	24.9	0.12	15.0
0.230	0.81	0.109	23.4	0.93	18.7
0.254	1.25	0.074	14.6	2.11	21.6
0.250	1.28	0.059	11.3	3.26	25.0
3.38	20.5	0.33	8.3	24.3	32.6
3.28	20.3	0.26	3.9	44.3	40.0
3.28	20.0	0.30	2.6	64.3	53.3
18.95	119.0	1.25	2.6	183.2	93.2

TABLE VII

Supported Platinum Black No. 1

In vacuum for two hours at 450°

1	2	3	4	5	6
0.246	0.03	0.242	25.3	0.03	8.0
0.236	0.18	0.209	18.2	0.21	15.0
0.250	1.11	0.084	14.5	1.28	18.0
3.33	21.1	0.19	8.4	22.3	23.3
30.20	190.0	1.80	2.6	212.3	86.5

On supported black No. 2 only one series of measurements with a 3 gram sample was made and is recorded in Table VIII.

TABLE VIII

Supported Platinum Black No. 2

In vacuum for two hours at 250°

1	2	3	4	5	6
0.236	0.48	0.164	33.6	0.48	5.33
0.236	1.34	0.036	19.0	1.61	7.65
0.236	1.32	0.039	8.8	3.01	8.0
3.32	21.87	0.06	8.4	25.0	10.0
10.60	68.5	0.40	6.2	93.5	23.4
18.20	117.5	0.80	4.9	210.	46.6

As seen from this and the preceding tables, the two blacks have somewhat different characteristics. While the initial values of the heats of adsorption are about the same, they decrease much more rapidly with the black No. 2. In agreement with this, the black No. 1 shows a stronger adsorption of hydrogen at low pressures while in the later portions of the adsorption isotherms the two samples behave more alike. Of some interest is a comparison of our results with those which were obtained by one of us (Ref. 1) using non-supported platinum blacks but prepared from the same grade of platinum and by identical methods. This comparison fully confirms those views on the action of the support material which have been repeatedly stressed by Taylor.[5] Namely, the support is found to increase many fold the adsorptive capacity per unit weight of the adsorbent and to stabilize the metal against the sintering action of high temperatures. The effect on the magnitude of the heats of adsorption is not pronounced, but perhaps slightly higher values result on the supported metal.

The unsupported platinum black. The adsorptive characteristics of three unsupported platinum blacks have been already studied by one of us (Ref. 1) in some detail. While the results there obtained seemed to be in complete agreement among themselves, they necessarily led to the conclusion that water vapor, though quite easily removed from the platinum surface, had extremely high heats of adsorption, at least on platinum prepared by precipitation from solution.

The present measurements were intended chiefly to test the correctness of the method previously employed in calculating the heats of adsorption of water vapor. It was intended to prepare a black by precipitation with formaldehyde, thus identical with the black No. 2 of the earlier publication and, first, to carry out a complete set of measurements of the heats of adsorption of hydrogen and oxygen and of the heats of their reaction on the surface, thus making possible an indirect calculation of the heat of adsorption of water vapor; and second, to measure directly this last quantity. An agreement of values thus obtained would have been an ample proof of the correctness of the method.

An unexpected complication was met in that it was impossible to reproduce the characteristics of the black previously studied. Although then two samples were tried which showed no diverging results and now three samples were made with only immaterially different characteristics, the new and the old preparations were found to be entirely different, even though the method of preparation was reproduced to the last detail. The only possible explanation of this behavior we see in the fact that while formerly a technical grade of platinum was employed, the new samples were made of a C.P. grade of platinum.

The following Tables IX to XVIII show typical series of measurements made with the new black. In order to measure directly the heat of adsorption of water vapor, the gas-measuring section of the apparatus was modified

[5] Taylor: Fourth Report on Catalyst Catalysis, J. Phys. Chem., 30, 145 (1926).

somewhat. Instead of burettes a system consisting of two glass bulbs was employed. One, maintained at 0°C., contained some liquid water distilled previously several times in vacuum. It communicated through a stopcock with another evacuated bulb of known volume and kept at 20°C. This latter communicated in turn through a stopcock, with the calorimeter vessel. Before each gas admission the stopcock between the bulbs was opened for at least a period of 10 minutes. In calculating the heats of adsorption it was assumed that the amount of water vapor admitted was equal to that contained in the second bulb at 20°C. and at a pressure equal to the saturation vapor pressure of water at 0°C. While the McLeod manometer connected to the calorimeter could not be used for measuring the pressure of water vapor, still it gave an indication whether any water vapor remained unadsorbed. Thus it was ascertained that the first one or two cc. (at N.T.P.) of water vapor were completely adsorbed by the platinum black. Accordingly, it was assumed in calculations that the adsorption was 100%. In case this assumption is not quite correct the values given below are lower than the true ones. Since the general trend of the adsorption curves as now studied does not differ materially from that described earlier by one of us, the following tables present only the more important features of each experiment, the middle sections, or the end of each being omitted. Tables IX to XII are a consecutive series of experiments. Between the last of these and the one represented in Table XIII a number of unsuccessful attempts to measure the heat of adsorption of water vapor was made and the black was heated to 250° intermittently for a very considerable number of hours. It showed at the end very marked sintering and it was deemed necessary therefore to repeat the whole series of hydrogen and oxygen adsorptions. These are given in Tables XIV to XVII. The last table is a run made with a newly prepared but otherwise quite similar sample.

TABLE IX

Unsupported Platinum Black No.1

Evacuated at 20°, heated in hydrogen to 250°, in vacuum for five hours at 250°

Hydrogen on a Bare Surface

1	2	3	4	5	6
0.195	0.28	0.169	59.6	0.22	0.58
0.195	0.36	0.162	55.5	0.45	1.19
0.195	0.39	0.150	50.2	0.78	1.72
0.195	0.33	0.164	42.7	1.05	2.56
0.195	0.32	0.165	4.14	1.25	2.85
0.195	0.41	0.157	36.6	1.48	3.76
0.195	0.37	0.160	29.6	1.76	4.00
0.195	0.41	0.157	37.0	1.98	4.50
.....					
10.43	30.0	7.62	24.5	81.5	195.50
12.67	31.9	9.67	25.4	106.	229.00
19.42	47.5	14.97	25.5	137.	284.50
6.99	23.0	4.83	15.9	146.	304.50

TABLE X

Unsupported Platinum Black No. 1
In vacuum for one hour at 0°
Oxygen on Hydrogen

1	2	3	4	5	6
0.192	0.023	0.190	65.4	0.013	0.636
0.192	0.015	0.190	78.2	0.03	1.27
0.192	0.03	0.189	73.0	0.04	1.90
0.237	0.02	0.235	61.2	0.06	2.69
0.192	0.01	0.191	64.0	0.07	3.34
3.01	0.21	2.99	53.6	0.25	13.30
.....					
3.02	1.28	2.90	50.7	2.5	91.2

TABLE XI

Unsupported Platinum Black No. 1
Treated with hydrogen at 250°, in vacuum for ten hours at 250°
Oxygen on a Bare Surface

1	2	3	4	5	6
0.196	0.015	0.195	85.0	0.015	0.65
0.196	0.015	0.195	79.8	0.030	1.30
0.196	0.015	0.195	77.5	0.045	1.95
0.196	0.015	0.195	84.3	0.060	2.60
.....					
0.196	0.050	0.191	64.4	0.74	27.60
3.00	0.47	2.96	74.0	1.06	37.50
3.00	12.15	2.86	45.7	9.46	44.80
2.90	30.25	0.12	0	39.25	45.80

TABLE XII

Unsupported Platinum Black No. 1
In vacuum for one hour at 0°
Hydrogen on Oxygen

1	2	3	4	5	6
0.196	0.136	0.183	55.3	0.136	0.613
0.196	0.14	0.183	54.0	0.25	1.23
0.196	0.14	0.183	55.3	0.39	1.84
0.196	0.20	0.177	48.3	0.59	2.43
0.196	0.23	0.174	47.7	0.82	3.01
.....					
2.98	4.7	2.55	40.7	9.8	33.33
2.98	5.4	2.47	37.1	12.2	42.50

TABLE XIII

Unsupported Platinum Black No. 1
Heated in hydrogen to 250°, in vacuum for five hours at 250°
Water Vapor on a Bare Surface

1	4	6
0.339	?	1.13
0.339	18.7	2.26
0.339	15.0	3.38
0.339	15.0	4.47
0.339	16.0	5.60
0.339	16.7	6.71
0.339	16.8	7.80
0.339	15.1	8.92

TABLE XIV

Unsupported Platinum Black No. 1
In vacuum for five hours at 250°
Hydrogen on a Bare Surface

1	2	3	4	5	6
0.202	0.29	0.175	26.4	0.28	0.587
0.202	0.29	0.154	23.7	0.57	1.17
0.202	0.28	0.176	23.2	0.80	1.77
0.202	0.23	0.180	21.5	1.07	2.36
0.202	0.25	0.179	21.5	1.32	3.29
0.202	0.23	0.180	20.4	1.55	3.55

TABLE XV

Unsupported Platinum Black No. 1
In vacuum for one hour at 0°
Oxygen on Hydrogen

1	2	3	4	5	6
0.21	0.05	0.205	108.3	0.05	0.674
0.21	0.02	0.208	108.3	0.07	1.36
0.21	0.015	0.208	85.5	0.085	2.07
0.21	0.02	0.208	79.8	0.105	2.71
0.20	0.025	0.198	84.0	0.13	3.40
0.21	0.015	0.208	64.8	0.145	4.15

TABLE XVI

Unsupported Platinum Black No. 1
Treated with hydrogen at 250°, in vacuum for ten hours at 250°
Oxygen on a Bare Surface

1	2	3	4	5	6
0.20	0.14	0.187	70.8	0.14	0.623
0.20	0.07	0.193	68.7	0.21	1.27
0.20	0.02	0.198	64	0.23	1.93
0.20	0.02	0.198	65.9	0.25	2.59
0.20	0.02	0.198	69.4	0.27	3.25
0.20	0.015	0.198	56.0	0.285	3.90

Table XVII

Unsupported Platinum Black No. 1
In vacuum for one hour at 0°
Hydrogen on Oxygen

1	2	3	4	5	6
0.202	0.164	0.187	42.7	0.164	0.623
0.202	0.13	0.190	36.2	0.29	1.25
0.202	0.125	0.190	33.7	0.41	1.89
0.202	0.12	0.191	31.0	0.53	2.68
0.202	0.12	0.191	29.5	0.65	3.40
0.202	0.23	0.190	34.0	0.88	4.02

Table XVIII

Unsupported Platinum Black No. 1
Heated in hydrogen to 250°, in vacuum for 3 hours at 250°
Water Vapor on Bare Surface

1	4	6
0.339	34,400	1.13
0.339	25,200	2.26
0.339	22,800	3.38
0.339	22,100	4.42

In comparison with a platinum black prepared by the same method and studied previously (Ref. 1) the one now investigated shows a much stronger adsorption of hydrogen and much weaker adsorption of oxygen. This is true both with respect to the amount adsorbed and the heats of adsorption involved. The characteristics of these two supposedly similar blacks differ much more indeed than the characteristics of the blacks made by different methods but from the same sample of platinum, as described previously (Ref. 1). One is thus led to the conclusion—not new by any means—that the purity of the material used plays at least as important a role in determining the surface properties of a finely dispersed metal as the method of its preparation.

The data here presented allow a double calculation of the heat of adsorption of water vapor. Thus this heat of adsorption is equal to the heat of reaction of one molecule of hydrogen with adsorbed oxygen plus one-half the heat of adsorption of oxygen minus the heat of gaseous reaction (+58,000 cal.) and it is also equal to one-half the heat of reaction of one molecule of oxygen with adsorbed hydrogen plus the heat of adsorption of hydrogen minus the heat of the gaseous reaction. While this deduction is strictly correct, in its application to the experimental data, some uncertainty exists as to which values of the respective measured heats should be taken into calculation. In the following table the calculation has been carried out under

the assumption that the first volumes of oxygen react with that hydrogen which is adsorbed on the most active parts of the surface and so forth. Another possible choice is to take the weighted averages of the heats of adsorption and of the reaction but the results so obtained are not very different from the averages of Table XIX. The calculations of Table XIX have been carried out using interpolated values for 1, 3 and 8 cc. of adsorbed or reacting gas and they are compared with the direct values for water vapor.

TABLE XIX

Comparison of calculated and measured heats of adsorption of water vapor

Gas adsorb.	Measured heats of Adsorption		Measured heats of Reaction		Heat of adsorption of H_2O Calcd. from		
	H_2	O_2	H_2 with adsorb. O_2	O_2 with H_2	H_2 with O_2	O_2 with H_2	Measured
Active surface (Tables IX to XII and XVIII)							
1 cc.	55,000	83,000	55,000	75,000	38,500	34,500	34,500
3 cc.	44,000	75,000	48,000	63,000	27,500	17,500	24,000
8 cc.	35,000	69,000	40,000	59,000	16,500	6,500	20,000*
Sintered surface (Tables XIII to XVII)							
1 cc.	25,000	72,000	39,000	105,000	17,000	19,500	21,000*
3 cc.	21,000	60,000	31,000	79,000	3,000	2,500	17,000
8 cc.							16,000

* Extrapolated.

The calculated and measured values show, on the whole, an extremely good agreement when all the uncertainties involved in these calculations are considered. The only serious discrepancies found are those of the later values on the sintered surface but they are of such a nature as to allow of an explanation assuming that water vapor produced in the later stages of the reaction is not completely adsorbed. A general objection might be raised on the grounds that while the measured heats of adsorption of water vapor refer to a bare surface, the calculated values were obtained with a surface nearly saturated with either oxygen or hydrogen. There are no data available however to support or reject this argument and we are inclined therefore to consider the agreement of Table XIX as not of accidental nature. Thus, although we were unable to reproduce the adsorptive characteristics of a platinum black described previously (Ref. 1) and to measure directly heats of adsorption of water vapor exceeding 70,000 cal., still Table XIX may be considered as strong evidence that the calorimetric method and calculation here employed lead to correct results and that it is possible under certain conditions to produce platinum blacks on which water vapor has such high heats of adsorption.

In conclusion we wish to express our thanks to Professor H. S. Taylor for his many valuable suggestions and criticisms while the work was in progress.

Summary

1. A modified all glass calorimeter with a multiple thermojunction has been described.

2. The heat of adsorption of hydrogen on reduced zinc-chromium oxide has been studied and it has been found that a maximum in the heat of adsorption curve can be obtained under certain conditions of heat treatment of the adsorbent. The intensity of the maximum runs parallel with the adsorptive capacity of the oxide preparation.

3. Heats of adsorption of hydrogen on two supported platinum blacks have been measured.

4. Heats of adsorption of hydrogen, oxygen and water vapor on a non-supported platinum black have been measured.

5. It has been shown that the values of the heat of adsorption of water vapor measured directly and calculated from the data on hydrogen and oxygen are in good agreement.

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